

LOW PERMEATION NYLON TUBE WITH ALUMINUM BARRIER LAYER

RELATED APPLICATIONS

This application is a continuation-in-part of U. S. Pat. Appln. S.N. 09/951,091 filed Sept. 13, 2001; and, filed concurrently with this continuation-in-part application is a continuation-in-part application of U.S. Pat. Appln. S.N. 09/951,091, U.S. Serial No. [unknown], docket no. 00-20b, to Smith, et al. entitled "Low Permeation High Density Polyethylene Tube with Aluminum Barrier Layer".

BACKGROUND OF THE INVENTION

The present invention relates to the field of tubes, and particularly to the field of automobile fuel and vapor transmission tubes having reduced permeability to such fuel and vapor. More particularly, the invention relates to multi-layer nylon fuel transport tubes which have a thin aluminum barrier layer between an inner conductive nylon tube and an outer non-conductive nylon tube, and to the use of such fuel transport tubes to reduce the amount of fuel vapor released to the atmosphere from motor vehicles. Recent environmental regulations imposed on the automotive and on the fuel delivery industries severely limit the amount of fuel vapor that can permeate from the fuel system of motor vehicles and from the fuel delivery hoses used to transport such fuels. For example, these regulations require that all new automobiles sold in states where this regulation are in effect must pass a vehicle permeation test designated as the S.H.E.D TEST, which measures the emissions, i.e., fuel vapors, from a motor vehicle with the engine not running. Under this regulation, a maximum of 2 grams of vapor emission per 24 hours period is allowable. Such emissions are those permeating from the fuel hoses and any other parts of the fuel supply system.

Typically, fuel transfer hoses, in the past, have been constructed of natural or synthetic rubber material such as butadiene-acrylonitrile rubber or the like. Other hoses have been constructed using a fluoroelastomer as an inner wall surface layer of the hose and some other material as the outer layer. Such hoses have a high permeability to fuel vapor. Attempts to produce fuel transport hoses with reduced permeability to fuel vapors have included the use of corrugated polyamide and fluorocarbon thermoplastic

tubes. However, these structures are presently considered to be only marginally effective to reduce the permeability of fuel vapors while being relatively expensive. Others have attempted to produce a fuel hose with reduced permeability to fuel vapors by using a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride terpolymer liner and a thicker layer of hexafluoropropylene-vinylidene fluoride copolymer or other suitable elastomer as the conductive inner part of the tube. For example, such hoses are discussed in U.S. Pat. Nos. 4,606,952 to Sugimoto and 5,430,603 to Albino et al. Such hose structures though have a tendency to wrinkle on the inner radius of the forming mandrel or pin causing an undesirable and discernable defect which may also exhibit a weakened area in the hose.

A number of prior art patents disclose flexible hoses incorporating metallic layers of one type or another to reduce permeability of various materials. Such disclosures appear, for example, in U.S. Pat. No. 318,458 to Fletcher, where there is disclosed a multi-layer tubular structure made from India rubber and having a tin foil liner. Other prior art patents such as U.S. Pat. Nos. 4,559,793 to Hane et al.; 4,758,455 to Campbell et al.; 5,182,147 to Davis; 5,271,977 to Echuca et al.; 5,360,037 to Lindstrom; and 5,398,729 to Spurgat have attempted similar methods to reduce permeability of fluids and/or gases through various tubes. Typically, such prior art hoses are constructed by coating a metal strip on both sides with an adhesive which may, for example, be an adhesive made from a copolymer of ethylene and a monomer having a reactive carboxyl group. Commonly assigned U.S. Pat. No. 6,074,717 to Little et al., and U.S. Pat. Nos. 4,779,673 and 5,488,975 to Chiles et al. disclose synthetic rubber hoses used for circulation of fluids in radiant heating systems in houses and businesses. Chiles 5,488,975 discloses a flexible heating system hose having an oxygen barrier layer which may be aluminum. U.S. Pat. No. 5,476,121 to Echuca et al teaches a low permeable rubber hose having a barrier layer of silver or silver alloy formed by wet plating or dry plating with ion plating or sputtering. None of these art references teach a flexible fuel hose having an aluminum barrier layer bonded to a conductive NBR inner tube and to an elastomeric adhesion layer which might serve as a cover, wherein the rubber layers are vulcanized to prevent delamination.

Choosing the right combination of materials to be used in the construction of fuel hoses, such as fuel filler hoses and fuel filler neck hoses is becoming more and more difficult. Therefore, an urgent need exists, particularly in the automotive and fuel delivery industries for a fuel hose which prevents permeation of fuels and vapor and which resists delamination under stress over long periods of time while maintaining manufacturing costs at an acceptable level.

SUMMARY OF THE INVENTION

The present invention provides a fuel tube for use in fuel systems which is constructed to prevent permeation of fuel vapor into the environment and to prevent delamination under stress for a long period of time. In accordance with the invention, the fuel hose has a layer of aluminum sandwiched between a conductive nylon inner tubular structure and an outer non-conductive nylon tubular structure which could serve as a cover for the fuel hose.

Nylon is a generic name for a family of polyamides generally characterized by the presence of the amide group, $-CONH$. Not all nylons are polyamide resins, nor are all polyamide resins nylons. Typically, nylons have been prepared in the past by the condensation of a dicarboxylic acid and a diamine. For example, nylon 66 is prepared by the condensation reaction of the six-carbon dicarboxylic acid, adipic acid and the six-carbon diamine, hexamethylenediamine. Nylon 610 is commonly prepared by the condensation reaction of sebacic acid, a 10-carbon dicarboxylic acid, and hexamethylenediamine. Other nylons such as nylon 4, nylon 6 and nylon 9 are obtained by polymerization of butyrolactam, caprolactam and 9-aminononanoic acid, respectively. Nylons generally have good electrical resistance, but readily accumulate static charges.

The nylons useful in the present invention include nylon 4, nylon 6, nylon 66, nylon 610, nylon 9, nylon 11, nylon 12, etc. The nylon used to construct the inner conductive tubular structure and the outer non-conductive layer may be the same or different. Preferably, nylon 12 is used in the invention to construct both the inner conductive tubular structure and the outer non-conductive layer. The nylon used to prepare the inner conductive tube will contain an agent which imparts conductivity to the nylon. Typically, the conductive agent is carbon black, but may be any conductive agent

or combination of conductive agents commonly recognized in the industry to provide conductivity to a rubber or plastic material. Examples of such conductive agents include elemental carbon, copper, silver, gold, nickel, and alloys of such metals. In a preferred aspect of the invention, the conductive agent is carbon in the form of fibers or fibrils. Such carbon fibers or carbon fibrils are more fully described in the detailed description of the invention. Although carbon fibers or carbon fibrils are particularly preferred as the conductive agent, metal fibers, mixtures of metal fibers and metal alloy fibers may also be used.

The outer non-conductive thermoplastic layer is constructed from a rubber or thermoplastic material such as nylon, chlorinated polyethylene; chlorosulfonated polyethylene; styrene-butadiene rubber; butadiene-nitrile rubber; nitrile-polyvinyl chloride; EPDM, neoprene; vinyl ethylene-acrylic rubber; acrylic rubber; epichlorohydrin rubber; copolymers of epichlorohydrin and ethylene oxide; polychloroprene rubber; polyvinyl chloride; ethylene-propylene copolymers; ultra high molecular weight polyethylene; high density polyethylene; chlorobutyl rubber; and blends thereof. Preferably, the outer non-conductive thermoplastic layer is formed from nylon and, most preferably from nylon 12.

In addition to the conductive nylon inner tube, the aluminum layer and the non-conductive nylon outer tube, the hose of the present invention may contain a first tie layer between the inner conductive nylon tubular structure and the aluminum barrier layer, and a second tie layer between the aluminum barrier layer and the outer non-conductive layer to prevent delamination of the layers. The tie layers, typically, are any of the tie layers known in the art which will adhere to the nylon conductive layer and the nylon or other material used to form the non-conductive layer to the aluminum barrier layer. A tie layer may be required or, at least desired, to prevent delamination of the inner nylon layer and the outer nylon or thermoplastic layer from the aluminum barrier layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of the invention comprising an aluminum barrier layer sandwiched between a conductive nylon inner tube and an non-conductive nylon outer tube;

Fig. 2 is an end view of the fuel tube shown in Fig. 1;
Fig. 3 is a perspective view of another embodiment of the present invention;
Fig. 4 is an end view of the fuel tube shown in Fig. 3;
Fig. 5 is a perspective view of still another embodiment of the present invention;
Fig. 6 is an end view of the fuel tube shown in Fig. 5;
Fig. 7 is a perspective view of yet another embodiment of the present invention;
Fig. 8 is an end view of the fuel tube shown in Fig. 7.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, a fuel transport tube is provided which not only meets present low permeability standards, but also exhibits increased resistance to delamination during extended use. A fuel hose manufactured in accordance with the present invention is illustrated in Figs. 1 and 2, wherein a fuel tube 10 has an inner tubular structure 12 comprising a conductive nylon, an aluminum barrier layer 14 surrounding the outermost surface of the conductive nylon tube 12, and a non-conductive nylon outer tubular structure 16 adjacent to and surrounding the outermost surface of the aluminum barrier layer 14.

It has been found that the hoses of the present invention significantly reduce the permeation of fuel vapor as well as providing for extended tube life due to the unique combination and tubular structure wherein a layer of aluminum 14 is sandwiched between an inner tubular structure 12 made from a conductive nylon and an outer tubular structure 16 made from a non-conductive nylon. The inner conductive nylon tubular structure 12 can have a wall thickness of up to about 2 mm. Preferably, the wall thickness of the inner conductive nylon tubular structure 12 is about 0.2 to 1.5 mm, and most preferably about 0.5 to 1.25 mm. The nylon component of the inner conductive nylon tubular structure 12 appears to be critical and, while other nylons may be used in the present invention, nylon 12 is preferred.

Typically, the inner conductive nylon tube 12 is rendered conductive by introducing a conductive agent into the nylon material prior to forming the inner tubular structure 12. The conductive agent 18 can be any of the conductive agents known in the art, such as elemental carbon, copper, silver, gold, nickel, and alloys of such metals or any combination of conductive agents which will provide the necessary conductivity

characteristic to the inner nylon tube 12. In a preferred aspect of the invention, the conductive agent 18 is carbon in the form of fibers or fibrils. Carbon fibers or carbon fibrils typically have a high ratio of length to diameter, e.g., on the order of several hundred to one. Carbon or graphite fibers normally have a diameter of several microns, most generally in the range of about 7 to 8 microns. The carbon or graphite fibrils have been described as extremely fine fiber or cell-like nano-particles formed during the first stages of gel formation. The amount of conductive agent 18 in the nylon material used to make the inner nylon tube 12 should be sufficient to provide effective conductivity, but not in excessive amounts which would tend to make the nylon difficult to process, and can range up to about 20 weight percent; however, the most effective amount of conductive agent 18 may vary, depending on the particular conductive agent 18 used. In a particular aspect of the invention, carbon black in an amount of about 2 to 20 weight percent has been found to be especially useful in carrying out the invention. Typically, the aluminum barrier layer 14 is a thin layer of aluminum having a thickness of about 0.02 to 1.5 mm. In a preferred aspect of the invention, the inner nylon tubular structure 12 is wrapped by a layer of aluminum foil 14. This may be accomplished by helical wrapping or by tensioned radial curling. Alternatively, a thin layer of aluminum 14 may be deposited around the outer surface of the inner nylon tubular structure 12 by electrolytic deposition.

According to the invention the outer surface of the aluminum barrier layer 14 is covered with a non-conductive nylon tube 16. The nylon material used to form the non-conductive nylon tube 16 can be the same nylon material used to form the conductive nylon tube 12 or it can be a different nylon. Typically, the non-conductive nylon tube 16 will have a wall thickness of about 0.25 to 1.5mm. Preferably, the wall thickness of the non-conductive nylon tube 16 is about 0.4 to 0.8mm.

Figs. 3 and 4 illustrate another embodiment of the invention where the hose 20 comprises an inner conductive nylon tube 22, an aluminum barrier layer 24, a first tie layer 23 between the inner conductive nylon layer 22 and the aluminum barrier layer 24, an outer non-conductive nylon tube 26, and a second tie layer 25 between the aluminum barrier layer 24 and the outer non-conductive nylon layer 26. As in the first embodiment, the inner conductive nylon tube of the second embodiment also contains a

conductive agent 18 which is preferably carbon black. The wall thickness of the tubular members and the aluminum barrier layer of the second embodiment is essentially the same as the thickness of the tubular members and the aluminum barrier layer of the first embodiment.

Figs. 5-8 illustrate another aspect of the invention, where the tubes of both the first embodiment and the second embodiment may also comprise an outer cover 28 adjacent to and surrounding the non-conductive nylon tubular structure 26 of the tube 10. The cover 28 is formed from a rubber or thermoplastic material such as nylon, chlorinated polyethylene; chlorosulfonated polyethylene; styrene-butadiene rubber; butadiene-nitrile rubber; nitrile-polyvinyl chloride; EPDM, neoprene; vinyl ethylene-acrylic rubber; acrylic rubber; epichlorohydrin rubber; copolymers of epichlorohydrin and ethylene oxide; polychloroprene rubber; polyvinyl chloride; ethylene-propylene copolymers; ultra high molecular weight polyethylene; high density polyethylene; chlorobutyl rubber; and blends thereof. Preferably, the cover is formed from chlorinated polyethylene (CPE). The particular material selected as the outer cover should be chosen according to the environmental condition the hose is expected to encounter. Typically, a thickness of about 0.25 to 1.25 mm is sufficient for the cover.

The particular tie layer used in the present invention may be any of the adhesive tie layers commonly known in the art and which will adhere to the nylon tubes to the aluminum layer. For example, anhydride-modified linear low density polyethylenes such as those available from DuPont under the name Bynel® or from Mitsui under the name Admer® have been found effective for the materials of the invention.

The adhesive tie layer used between the inner conductive nylon tube and the aluminum barrier layer may be different from the adhesive used between the outer non-conductive nylon tube and the aluminum barrier layer. Some adhesive tie layers exhibit better stability toward hydrocarbon fuels than other adhesives, and some adhesives have better adhesion properties than others. Therefore, it may be desirable to use an adhesive tie layer having good hydrocarbon fuel stability between the inner conductive layer and the aluminum barrier layer even though other adhesive tie layers may adhere better to the nylon and the aluminum, whereas, one may choose an adhesive tie layer having better adhesion characteristics and less stability toward hydrocarbon fuels to

adhere the outer non-conductive nylon to the aluminum layer since this adhesive would be on the opposite side of the aluminum barrier layer and, therefore, would not be subjected to the hydrocarbon fuel vapors.

The method of producing the fuel transfer hose of the first embodiment of the present invention comprises the steps of:

- forming a first non-conductive nylon tube;

- wrapping a thin layer of aluminum foil around the outer surface of the nylon tubular structure; and

- forming an outer non-conductive tube around the aluminum barrier layer.

Typically, the inner conductive nylon tube and the outer non-conductive nylon tube are formed by extrusion techniques known in the art. The application of the aluminum barrier layer on the inner conductive tube is accomplished by helical wrapping or by tensional radial curling or by any other method by which the aluminum foil can be applied around the nylon tubular structure. Another method for applying the aluminum layer or the nylon tubular structure is by electrolytic deposition. The non-conductive nylon layer can be applied around the aluminum coated nylon tubular structure by extrusion techniques known in the art. Other additives such as antioxidants, processing aids, etc., can be employed in amounts and methods known in the art.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent to those skilled in the art that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.